

Measurement of Mixed Micelle Size by Dynamic Light Scattering

Many applications of surfactants involve mixtures. Indeed, surfactants are typically impure so that even single materials may be considered mixtures. One particularly typical combination is that of ionic and nonionic surfactants. While the former are highly detergent, the latter exhibit less foaming, more resistance to precipitation on cooling or on addition of divalent cations, and less skin irritation.

Mixed surfactants generally form mixed micelles. The size or aggregation number (N) of these micelles is an indication of their efficiency for solubilization and also correlates with the viscosities of their solutions. However, the size of the mixed micelle is not simply an average of the sizes of the two 'pure' micelles.

The dimensions of mixed micelles of a nonionic surfactant, Triton X-100 (TX100) and sodium dodecyl sulfate (SDS) were determined with the DynaPro-801 using the method of Cumulants. The total surfactant concentration was maintained at 20 mM, which is 100 times larger than the critical micelle concentration, and the ratio of anionic to nonionic was varied. The ratio is reported as the mole fraction of SDS (Y). Measurements were performed at moderate, intermediate, and high ionic strengths (100, 400, and 600 mM, respectively) adjusted with NaCl.

Figure 102-1 shows the apparent radius as a function of composition for three ionic strengths.

As evident in the figure, the ionic strength has very little effect on R_H for TX100, while the salt effect is dramatic for both the mixed micelles and SDS alone. In particular, micelle size diminishes monotonically with anionic content at low salt, but passes through a maximum at high salt. Mixed micelle size decreases with increase in Y in 100 mM NaCl, increases strongly with Y in 600 mM NaCl, and is virtually independent of Y for $0.3 < Y < 0.8$ in 400 mM NaCl.

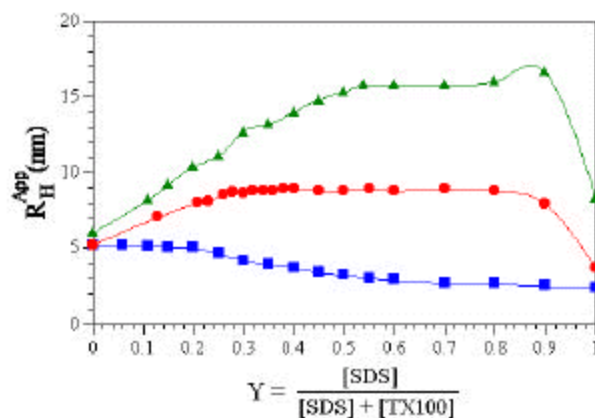


Figure 102-1: Hydrodynamic radius of mixed micelles as a function of mole fraction SDS (Y) in 100 (B), 400 (J), and 600 (H) mM NaCl.

The above results can be understood in terms of effective surfactant head group area. For geometric reasons, larger surfactant head groups correspond to smaller N , in that fewer surfactant molecules are required to produce a micelle of the same size. For ionic surfactants, the effective head group size includes a contribution arising from electrostatic repulsion. For this reason, micelle size increases with added salt for pure SDS ($Y = 1$). When repulsive forces dominate, i.e. at low ionic strength, the effective head group size of SDS is larger than that of TX100. This is why N increases upon TX100 addition in 100 mM NaCl until Y diminishes to < 0.15 (right to left in Figure 3). For $Y < 0.15$, the SDS groups are too far apart to repel each other.

At high salt, the range of electrostatic effects diminishes, and the effective head group size of SDS is small compared to that of TX100. Consequently, micelles grow upon addition of SDS up to $Y = 0.9$. Under these conditions however, repulsive effects begin to contribute, and a subsequent drop in N is observed upon further increase in Y .

